Paper

Syntheses, Solid State Structures and Photochemistry of α , ω -Bis-[(1,8-dichloroanthracen-10-yl)dimethylsilyl]alkanes

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Abstract Starting from 10-bromo-1,8-dichloroanthracene, a series of 1,8-dichlorinated anthracene derivatives, flexibly bridged in position 10 by $-Me_2Si-$ and $-Me_2Si-(CH_2)_n-SiMe_2-$ linker units, were synthesised. The linked anthracenes were generated by converting (1,8-dichloroanthracen-10-yl)lithium with chlorosilanes in salt-elimination reactions. The bichromophors were tested in UV light induced photo reactions. None of the new compounds yielded any intra- or intermolecular photoproduct. All α , ω -(dimethylsilyl)alkane-linked bisanthracenes decomposed to give 1,8-dichloro-9-hydroxyanthracen-10(9H)-one in the presence of oxygen. A completely different behaviour was shown by the bisanthracenyldimethylsilane, undergoing a 9,10:3',4'-photocyclomerisation reaction. The new compounds were characterised by NMR spectroscopy, mass spectrometry and in most cases by X-ray diffraction studies.

Key words anthracenes, salt metathesis reactions, solid-state structures, photocyclomerisation, oxygenation

Functionalised anthracenes provide a non-flexible framework with well-defined distances and orientation of the substituents (e.g., in positions 1 and 8 or 9 and 10). Therefore, such systems are useful building blocks and they are widely used in many fields of (metal)organic chemistry.^{1,2} The number of directed functionalities for further modification can be increased by linking two anthracene units, for example, in position 10.

An interesting literature-known example for these bichromophoric systems are the polyoxyethylene-linked anthracenes **A** (Figure 1), which can be used as photo-switchable crown ether molecules.³ However, for our research in the field of poly-Lewis acids, it is necessary to work with strictly donor-free anthracene derivatives. Recently, we connected two 1,8-dichloroanthracene systems by rigid linker units to construct non-flexible frameworks bearing four directed chlorine functions.⁴ Certainly, most of these products are barely soluble and therefore not applicable for further functionalisation.

-3, 6

9,10:3'.4'

9,10:1',4



Figure 1 Examples of anthracene-containing bichromophoric systems **A** and **B**.^{3,5} The syntheses of the flexibly linked dichloroanthracenes **C** and **D** are presented in this paper.

An example for well-soluble bisanthracenes without any donor atoms are the α,ω -bis[(dianthracen-9-yl)dimethylsilyl]alkanes **B**,⁵ which are available in two step syntheses from dihydroanthracene and the corresponding α,ω bis(chlorodimethylsilyl)alkane. Since this class of compounds is limited to non-substituted anthracenes so far, we herein report the synthesis of 1,8-dichlorinated anthracenes, connected by $-Me_2Si-$ and $-Me_2Si-(CH_2)_n-SiMe_2$ linker units (**C** and **D**). Starting from 10-bromo-1,8-dichloroanthracene, they were built up in one-step salt elimination reactions. All products were tested in UV irradiation experiments and two (photo)products were characterised comprehensively.

Starting from 10-bromo-1,8-dichloroanthracene (1),⁶ compounds **2–7** were obtained in salt metathesis reactions (Scheme 1). The six new α,ω -bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]alkanes were obtained in low to moderate yields and characterised by multinuclear NMR spectros-copy and high-resolution mass spectrometry.



Scheme 1 Syntheses of the linked 1,8-dichloroanthracenes **2–10**. *Reagents and conditions:* i) 1. *n*-BuLi, THF, –78 °C, 1.5 h, 2. Me₂SiCl₂, –78 °C to r.t., 41%; ii) 1. *n*-BuLi, THF, –78 °C, 1.5 h, 2. Me₂ClSi–X–SiClMe₂, –78 °C to r.t., 45% (**3**), 30% (**4**), 52% (**5**), 57% (**6**), 33% (**7**), 29% (**8**); iii) 1. *n*-BuLi, THF, –78 °C, 1.5 h, 2. Me₂SiCl(CH₂)_{*n*}CH=CH₂, –78 °C to r.t., 94% (**9**), 62% (**10**).

Bromoanthracene **1** was further reacted with chlorodimethylvinylsilane and the corresponding allyl derivative affording compounds **9** and **10** (Scheme 1). Aiming at the generation of semi-flexible linker units, both alkenylsilylsubstituted anthracenes were attempted to be converted in olefin metathesis reactions using Grubbs I catalyst in dichloromethane. However, no metathesis reactivity was observed in both cases. Upon reacting the allyl-substituted species **10** in a non-inert atmosphere, small amounts of a bright yellow solid were obtained, which was proven to be disiloxane **8**. Attempts to obtain **8** in similar reactions without using Grubbs I catalyst did not succeed. A more efficient way to generate compound **8** is the direct conversion of lithiated **1**,8-dichloroanthracene with **1**,3-dichlorotetramethyldisiloxane.

Single crystals, suitable for X-ray diffraction experiments, of all new compounds were obtained, except for the propane derivative **6**. Due to their similar substitution pattern the structures of the bisanthracenes **2–5** and **7** compare very well. Exemplarily, the molecular structures of **3** and **5** are displayed in Figure 2 [see Figures S1–S5 in Supporting Information (SI) for solid state structures of **2**, **4** and 7-10]. For all five compounds the chlorine atoms are inplane with the corresponding aromatic system. The substituents in position 10 are out of plane of the anthracene backbone they are bonded to. The torsion angles C(8)-C(9)-C(10)–Si(1) and C(12)–C(11)–C(10)–Si(1) range from –11.1(1)° and 10.2(2)° (both for **2**) to -21.0(2)° and 21.9(2)° (both for 7) demonstrating the bending of the substituents. They result from intramolecular repulsive interactions between the hydrogen atoms of the Si-bound methyl groups and the hydrogen atoms located at positions 4 and 5 of the anthracene skeleton. In the case of compound **3**, these hydrogenhydrogen distances are found to be 2.1(1)-2.2(1) Å. Due to these interactions, the bonds C(10)-Si(1) are remarkably elongated [1.90(1) and 1.92(1) Å] compared to the standard C-Si bond length (1.84 $Å^7$). The same trends in terms of the bending of the substituents as well as the elongation of the bond C_{Ant}-Si are observed for the corresponding values of 1,8-dichloro-10-(trimethylsilyl)anthracene and are thus an inherent molecular property.6

As shown in Figure 2, different configurations of the flexibly linked bisanthracenes can be observed in the solid state. It is worth mentioning that compounds 3 and 4 with rather short linker units crystallise in a folded configuration bearing four directed chloro substituents. However, for compounds 5 and 7 with longer linker units a stretched configuration seems to be preferred in the solid state. This behaviour can be illustrated by comparison of the torsion angles C(3)-Si(1)-Si(2)-C(17) for compound **3** [-6.7(1)°] and C(3)–Si(1)–Si(1')–Si(3') for compound **5** (180.0°). In the case of the folded molecules, very short intramolecular π - π interactions are observed. For compound 3 the shortest intramolecular centroid-centroid distance is located between the mean planes of C(1)-C(2)-C(11)-C(12)-C(13)-C(14)and C(16)–C(17)–C(18)–C(23)–C(24)–C(25) with 3.51(1) Å. In the structure of compound **5** only intermolecular π - π interactions are found. The shortest one is located between the mean planes of C(1)-C(2)-C(11)-C(12)-C(13)-C(14)and C(4)-C(5)-C(6)-C(7)-C(8)-C(9) with 3.63(1) Å.

Bouas-Laurent et al. have shown that in the case of nonsubstituted anthracenes, short linkers containing dimethylsilvl groups induce a 9,10:1',4'-photocyclomerisation.⁸ When the chloro-substituted anthracene derivatives 3-7 were investigated concerning photocyclomerisation reactions (λ = 365 nm) using dried and degassed solvents, no conversion was observed at all. Apparently, the expected 9,10:1',4'-photocyclomerisation yielding E-type compounds (Scheme 2) is inhibited by the chloro substituents in position 1. Using non-dried and oxygen-containing chloroform instead, oxygenation reactions take place and 1,8dichloro-9-hydroxyanthracen-10(9H)-one (11) was quantitatively obtained in all five cases (Scheme 2). Further experiments offered a slightly slower formation of compound 11 even without additional UV irradiation, for example, when the samples were exposed to sunlight. We assume that the



Figure 2 Molecular structures of 1,2-bis(1,8-dichloroanthracen-10-yl)-1,1,2,2-tetramethyldisilane (**3**, above) and 1,2-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (**5**, below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles for **3/5**: C(1)-C(2) 1.432(2)/1.432(2), C(1)-C(1) 1.737(4)/1.738(1), C(2)-C(11) 1.442(5)/1.440(2), C(10)-C(11) 1.417(5)/1.422(2), C(10)-Si(1) 1.919(4)/1.919(1), C(17)-C(17') -/1.544(2), C(17)-Si(1) -/1.886(1), Si(1)-Si(2) 2.387(2)/-, C(1)-C(2)-C(11) 118.4(3)/118.2(1), C(2)-C(11)-C(10) 121.4(3)/120.6(1), C(10)-Si(1)-C(17) -/112.6(1), C(10)-Si(1)-Si(2) 109.3(1)/-, C(11)-C(10)-Si(1) 116.6(3)/120.3(1).

initial product is an endoperoxide, formed by the reaction of the anthracene-backbone with oxygen. In a second step, the C_{Ant}–Si bond is hydrolysed, followed by the heterolytic cleavage of the O–O bond, yielding compound **11**. Evidence for the postulated mechanism stems from GC/MS-data of the raw products, showing the formation of small (cyclic) siloxanes. Comparable results were obtained by Linker et al. for the base-catalysed decomposition of anthracene endoperoxides.⁹



Scheme 2 UV irradiation of bisanthracenes **3–7**, which do not yield any intramolecular photoproducts like **E** or **F** but decompose to 1,8-dichloro-9-hydroxyanthracen-10(9*H*)-one (**11**) in the presence of oxygen and moisture.

Compound **11** was identified by NMR spectroscopy, mass spectrometry and X-ray diffraction experiments. Its molecular structure in crystalline state is depicted in Figure S6 (SI). No unexpected structural parameters are found in the molecule. The C–C, C–Cl and C=O bond lengths of **11** are identical within experimental errors with those of 1,8-dichloro-10-anthrone.¹⁰

A completely different behaviour is observed for the bisanthracenyldimethylsilane **2**. After irradiation with UV light in the absence of oxygen, the 9,10:3',4'-photocyclomerisation product **12** (Scheme 3) was found to be formed in quantitative yield. Bouas-Laurent et al. found the analogous $[4\pi+2\pi]$ cyclomer for the non-chlorinated derivative.¹¹ The complexity of **12** is illustrated by NMR spectroscopy. Sixteen signals in the ¹H NMR spectrum, one each for the protons of the methyl groups, are observed. Due to their multiplicity and by means of 2D NMR methods, we were able to assign all resonances. A characteristic doublet of doublet of doublet sis found for the proton in position 3' at 3.39 ppm.

D

It shows couplings to the protons in position 2' (6.21 ppm, ${}^{3}J_{H,H} = 4.0 \text{ Hz}$), 4' (3.95 ppm, ${}^{3}J_{H,H} = 12.0 \text{ Hz}$) and 9 (5.56 ppm, ${}^{3}J_{H,H} = 2.5 \text{ Hz}$).



Scheme 3 UV irradiation of bisanthracene **2**. The 9,10:3'4'-photocyclomer **12** is formed quantitatively. Also shown is the literature-known compound G^{12} as an example for this kind of photocyclomerisation products.

Single crystals of the 9,10:3',4'-photocyclomer 12, suitable for X-ray diffraction experiments, were obtained upon slow evaporation of a saturated benzene solution. The molecular structure of 12 contains a 2,3-dihydrobarrelene motive,¹³ with the bridgehead atoms C(1) and C(8) (Figure 3). The bonds C(1)–C(2), C(1)–C(14), C(8)–C(7) and C(8)–C(9) have lengths between 1.51 and 1.53 Å. Compared to them, the newly formed bonds are apparently longer at 1.57 Å for C(8)–C(28) and 1.59 Å for C(1)–C(15). Furthermore, the formation of a C–C-single bond between C(15) and C(28) is indicated by its length of 1.544(2) Å. The lengths of the bonds C(2)–C(7) [1.403(2) Å] and C(9)–C(14) [1.405(2) Å] are similar to values of previously studied chloro-substituted triptycenes.¹⁴ With values ranging from 1.86 Å [for Si(1)–C(30)] to 1.92 Å [for Si(1)–C(1)] the four Si–C bonds exhibit strong variations. The bond angles at Si(1) range from 91.0° for C(1)-Si(1)-C(17) to 118.7° for C(1)-Si(1)-C(30). This distortion from tetrahedral geometry and the different Si-C bond lengths are probably consequences of the unsymmetrical photocyclomerisation and the formation of a five-membered ring.

Although there are several examples for analogous 9,10:3',4'- (or 9,10:1',2'-)photocyclomers like compound **12**,^{11,15} only two corresponding compounds were crystallised and characterised in the solid state so far.^{12,16} The 9,10:1',2'-photocyclomer of methyl-2,2-di(anthracen-9yl)glycolate **G** (Scheme 3) is the only compound with a onemembered linker unit between the anthracene moieties and therefore suitable to be compared with **12**. Almost all bond lengths of compound **12** are the same as the corresponding ones of the glycolate within experimental error.¹² Deviations only exist for the bonds C(1)–C(15), C(15)–C(16)



Figure 3 Molecular structure of the 9,10:3',4'-photocyclomerisation product 12 of bis(1,8-dichloroanthracen-10-yl)dimethylsilane in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)-C(2) 1.531(2), C(1)-C(14) 1.517(2), C(1)-C(15) 1.590(2), C(1)-Si(1) 1.921(2), C(2)-C(7) 1.403(2), C(7)-C(8) 1.509(2), C(8)-C(9) 1.517(2), C(8)-C(28) 1.568(2), C(9)-C(14) 1.405(2), C(15)-C(16) 1.512(2), C(15)-C(28) 1.544(2), C(16)-C(17) 1.375(2), C(17)-Si(1) 1.890(2), C(30)-Si(1) 1.859(2); C(1)-C(2)-C(7) 113.3(1), C(1)-C(15)-C(16) 105.4(1), C(1)-C(15) 112.2(1), C(1)-Si(1)-C(17) 91.0(1), C(1)-Si(1)-C(17) 115.6(1), C(15)-C(28)-C(27) 114.6(1), C(16)-C(17)-Si(1) 107.5(1).

and C(16)-C(17), which are part of the five-membered ring. These bonds are elongated for compound **12** due to the bulky Si atom in its linker unit.

In conclusion, 10-bromo-1,8-dichloroanthracene has been used as a starting material in salt-elimination reactions to synthesise a series of 1,8-dichlorinated anthracene derivatives linked in position 10. The flexible linker units $[-Me_2Si- and -Me_2Si-(CH_2)_n-SiMe_2-]$ do not contain any donor atoms. Despite of the chain length, no intra- or intermolecular cycloaddition products were obtained in UV-irradiation experiments for the α, ω -bis(dimethylsilyl)alkanelinked compounds. However, 1,8-dichloro-9-hydroxyanthracen-10(9H)-one was formed as a decomposition product in the presence of oxygen in all cases. Irradiation of bis(1,8-dichloroanthracen-10-yl)dimethylsilane instead led to the formation of the corresponding 9,10:3',4'-photocyclomerisation product, which was also obtained for the non-chlorinated derivative in previous experiments.¹¹ The solid structures of the decomposition product and the photocyclomer were determined by X-ray diffraction experiments.

10-Bromo-1,8-dichloroanthracene $(1)^6$ and bis(chlorodimethylsilyl)methane¹⁷ were synthesised according to literature protocols. For the synthesis of 1,3-bis(chlorodimethylsilyl)propane and 1,6-bis-(chlorodimethylsilyl)hexane, see SI. Dimethylvinylchlorosilane, 1,2dichloro-1,1,2,2-tetramethyldisilane, 1,2-bis(chlorodimethylsilyl)eth-

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ane (all from abcr), allyldimethylchlorosilane, dichlorodimethylsilane and 1,3-dichlorotetramethyldisiloxane (all from Alfa Aesar) were used without further purification. First-generation Grubbs catalyst was purchased from Strem Chemicals. All reactions were carried out under an anhydrous, inert atmosphere of N₂ using standard Schlenk techniques in anhydrous THF (dried over potassium). The solvent was freshly distilled before being used for the reactions. Column chromatography was performed on silica gel 60 (0.04–0.063 mm). NMR spectra were recorded on a Bruker Avance III 300, a Bruker DRX 500, a Bruker Avance III 500 and a Bruker Avance III 500 HD at ambient temperature (298 K). The chemical shifts (δ) were measured in ppm with respect to the solvent (CDCl₃: ¹H NMR δ = 7.26 ppm, ¹³C NMR δ = 77.16 ppm) or referenced externally (²⁹Si: SiMe₄). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. MALDI-TOF experiments were performed using a Voyager DE Instrument (PE Biosystems GmbH, Weiterstadt, Germany). High-resolution MALDI-TOF mass spectra were recorded with a Fourier Transform Ion Cyclotron resonance (FT-ICR) mass spectrometer APEX III (Bruker Daltonik GmbH, Bremen, Germany). Electrospray ionisation (ESI) experiments were performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters, Manchester, UK) in resolution mode, interfaced to a nano-ESI ion source. The numbering scheme for NMR assignments of the anthracenes (Figure 4) is based on IUPAC guidelines.



Figure 4 Anthracene numbering scheme, exemplarily shown for 1,8,10-substituted anthracene derivatives

Anthracene Derivatives 2-10; General Procedure

A solution of *n*-BuLi (1.6 M in *n*-hexane) was added dropwise to a THF solution of 10-bromo-1,8-dichloroanthracene (1) at -78 °C. The dark red mixture was stirred for 1.5 h at this temperature. The corresponding (di)chloro(di)silane was slowly added and the mixture was allowed to warm to r.t. After stirring overnight and quenching with H₂O, the aqueous layer was extracted with CH₂Cl₂ and the combined organic phases were dried (MgSO₄). The solvent was evaporated and the brownish-yellow crude product was purified by either sublimation, washing with CH₂Cl₂ or *n*-pentane, or column chromatography on silica gel.

Bis(1,8-dichloroanthracen-10-yl)dimethylsilane (2)

Synthesised according to the general procedure using 10-bromo-1,8dichloroanthracene (1; 450 mg, 1.38 mmol), *n*-BuLi solution (0.85 mL, 1.4 mmol) and dichlorodimethylsilane (0.080 mL, 0.66 mmol). Washing the crude product with *n*-pentane (3×10 mL) afforded **2** as a yellow solid; yield: 148 mg (41%).

¹H NMR (500 MHz, CDCl₃): δ = 9.48 (s, 2 H, H9), 8.34 (d, ³J_{H,H} = 9.0 Hz, 4 H, H4/H5), 7.53 (d, ³J_{H,H} = 7.1 Hz, 4 H, H2/H7), 7.14 (dd, ³J_{H,H} = 9.0, 7.1 Hz, 4 H, H3/H6), 1.26 (s, 6 H, 2 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 139.0 (C10), 137.1, 133.6, 129.4, 126.9 (C4/C5), 125.7 (C3/C6), 125.7 (C2/C7), 124.6 (C9), 8.4 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -7.8.

MS (MALDI-TOF, + ions, ABS): $m/z = 584.0 [M]^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for C₃₀H₂₀Cl₄Si⁺: 548.0088; measured: 548.0096, dev. [ppm]: 1.39, dev. [mmu]: 0.76.

1,2-Bis(1,8-dichloroanthracen-10-yl)-1,1,2,2-tetramethyldisilane (3)

Synthesised according to the general procedure using 10-bromo-1,8-dichloroanthracene (**1**; 450 mg, 1.38 mmol), *n*-BuLi solution (0.85 mL, 1.4 mmol) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (0.12 mL, 0.64 mmol). Washing the crude product with *n*-pentane (3×5 mL) and CH₂Cl₂ (3 mL) afforded **3** as a yellow solid; yield: 177 mg (45%).

¹H NMR (500 MHz, CDCl₃): δ = 9.22 (s, 2 H, H9), 8.01 (d, ³*J*_{H,H} = 8.8 Hz, 4 H, H4/H5), 7.39 (d, ³*J*_{H,H} = 7.2 Hz, 4 H, H2/H7), 6.96 (dd, ³*J*_{H,H} = 8.8, 7.2 Hz, 4 H, H3/H6), 0.82 (s, 12 H, 4 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 137.7, 136.8 (C10), 133.0, 128.6, 127.0 (C4/C5), 124.9 (C2/C7), 124.5 (C3/C6), 123.4 (C9), 3.7 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -17.6.

MS (MALDI-TOF, + ions, DCTB): $m/z = 606.0 \text{ [M]}^+$, 303.0 [$C_{16}H_{13}\text{SiCl}_2$]⁺, 268.0 [$C_{16}H_{13}\text{SiCl}$]⁺.

HRMS (MALDI-TOF): m/z calcd for $C_{32}H_{26}Si_2Cl_4^*$: 606.03217; measured: 606.0322, dev. [ppm]: 0.05, dev. [mmu]: 0.03.

Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]methane (4)

Synthesised according to the general procedure using 10-bromo-1,8-dichloroanthracene (1; 450 mg, 1.38 mmol), *n*-BuLi solution (0.85 mL, 1.4 mmol) and bis(chlorodimethylsilyl)methane (0.13 mL, 0.66 mmol). Washing the crude product with *n*-pentane (3×5 mL) afforded **4** as a yellow solid; yield: 126 mg (30%).

¹H NMR (500 MHz, CDCl₃): δ = 8.90 (s, 2 H, H9), 7.85 (d, ${}^{3}J_{H,H}$ = 9.0 Hz, 4 H, H4/H5), 7.37 (d, ${}^{3}J_{H,H}$ = 7.1 Hz, 4 H, H2/H7), 6.86 (dd, ${}^{3}J_{H,H}$ = 9.0, 7.1 Hz, 4 H, H3/H6), 1.10 (s, 2 H, CH₂), 0.82 (s, 12 H, 4 × CH₃).

 $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl₃): δ = 137.0, 136.0 (C10), 133.3, 128.3, 126.9 (C4/C5), 124.9 (C2/C7), 124.3 (C3/C6), 123.9 (C9), 9.3 (CH_2) 7.5 (CH_3).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -5.0.

MS (MALDI-TOF, + ions, DCTB): *m*/*z* = 620.0 [M]⁺.

HRMS (MALDI-TOF): *m/z* calcd for C₃₃H₂₈Si₂Cl₄⁺: 620.04782; measured: 620.0468, dev. [ppm]: 1.65, dev. [mmu]: 1.02.

1,2-Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (5)

Synthesised according to the general procedure using 10-bromo-1,8dichloroanthracene (**1**; 430 mg, 1.33 mmol), *n*-BuLi solution (0.80 mL, 1.3 mmol) and 1,2-bis(chlorodimethylsilyl)ethane (135 mg, 0.63 mmol). Column chromatography on silica gel (\emptyset = 3 cm, *l* = 14 cm, eluent: *n*-pentane) afforded **5** as bright yellow crystals; R_f = 0.3 (*n*-pentane), yield: 207 mg (52%).

¹H NMR (500 MHz, CDCl₃): δ = 9.34 (s, 2 H, H9), 8.06 (d, ³J_{H,H} = 9.0 Hz, 4 H, H4/H5), 7.52 (d, ³J_{H,H} = 7.1 Hz, 4 H, H2/H7), 7.11 (dd, ³J_{H,H} = 9.0, 7.1 Hz, 4 H, H3/H6), 0.99 (s, 4 H, CH₂CH₂), 0.59 (s, 12 H, 4 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 138.2, 136.7 (C10), 133.2, 129.0, 127.5 (C4/C5), 125.4 (C2/C7), 124.7 (C3/C6), 124.0 (C9), 12.2 (SiCH₂), 3.2 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -0.8.

MS (EI, 70 eV): $m/z = 636.1 \text{ [M]}^+$, 388.1 [C₂₀H₂₃Cl₂Si₂]⁺, 330.1 [C₁₈H₁₇-Cl₂Si]⁺, 303.1 [C₁₆H₁₃Cl₂Si]⁺ 268.1 [C₁₆H₁₃ClSi]⁺.

HRMS (EI): *m/z* calcd for C₃₄H₃₀Cl₄Si₂⁺: 634.06347; measured: 634.06644, dev. [ppm]: 4.69, dev. [mmu]: 2.97.

1,3-Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]propane (6)

Synthesised according to the general procedure using 10-bromo-1,8dichloroanthracene (**1**; 433 mg, 1.33 mmol), *n*-BuLi solution (0.80 mL, 1.3 mmol) and 1,3-bis(chlorodimethylsilyl)propane (140 mg, 0.61 mmol). Column chromatography on silica gel (\emptyset = 3 cm, *l* = 14 cm, eluent: *n*-pentane) afforded **6** as bright yellow crystals; *R*_f = 0.2 (*n*-pentane); yield: 229 mg (57%).

¹H NMR (500 MHz, CDCl₃): δ = 9.31 (s, 2 H, H9), 8.06 (d, ³*J*_{H,H} = 9.0 Hz, 4 H, H4/H5), 7.53 (d, ³*J*_{H,H} = 7.1 Hz, 4 H, H2/H7), 7.16 (dd, ³*J*_{H,H} = 9.0, 7.1 Hz, 4 H, H3/H6), 1.48–1.53 (m, 2 H, SiCH₂CH₂), 1.17–1.23 (m, 4 H, 2 × SiCH₂), 0.50 (s, 12 H, 4 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 138.0, 137.3 (C10), 133.3, 129.0, 127.6 (C4/C5), 125.3 (C2/C7), 124.7 (C3/C6), 124.0 (C9), 23.4 (SiCH₂), 19.7 (SiCH₂CH₂), 3.8 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -3.3.

MS (EI, 70 eV): m/z = 650.1 [M]⁺, 303.0 [C₁₆H₁₃Cl₂Si]⁺, 268.0 [C₁₆H₁₃Cl-Si]⁺.

HRMS (EI): *m/z* calcd for C₃₅H₃₂Cl₄Si₂⁺: 648.07912; measured: 648.07776, dev. [ppm]: 2.10, dev. [mmu]: 1.36.

1,6-Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]hexane (7)

Synthesised according to the general procedure using 10-bromo-1,8dichloroanthracene (**1**; 433 mg, 1.33 mmol), *n*-BuLi solution (0.80 mL, 1.3 mmol) and 1,6-bis(chlorodimethylsilyl)hexane (165 mg, 0.61 mmol). Column chromatography on silica gel ($\emptyset = 3$ cm, l = 11cm, eluent: *n*-pentane) and washing the solid obtained with CH₂Cl₂ afforded **7** as bright yellow crystals; $R_f = 0.2$ (*n*-pentane); yield: 238 mg (33%).

¹H NMR (500 MHz, CDCl₃): δ = 9.43 (s, 2 H, H9), 8.29 (d, ³J_{H,H} = 9.0 Hz, 4 H, H4/H5), 7.59 (d, ³J_{H,H} = 7.2 Hz, 4 H, H2/H7), 7.35 (dd, ³J_{H,H} = 9.0, 7.2 Hz, 4 H, H3/H6), 1.16–1.29 (m, 8 H, 2 × SiCH₂CH₂CH₂), 1.04–1.09 (m, 4 H, 2 × SiCH₂), 0.61 (s, 12 H, 4 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 138.2, 138.0 (C10), 133.3, 129.2, 127.9 (C4/C5), 125.5 (C2/C7), 124.9 (C3/C6), 124.0 (C9), 33.0 (CH₂), 24.2 (CH₂), 19.5 (SiCH₂), 3.5 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -2.7.

MS (EI, 70 eV): $m/z = 692.1 \text{ [M]}^+$, 303.0 [C₁₆H₁₃Cl₂Si]⁺, 268.1 [C₁₆H₁₃Cl-Si]⁺.

HRMS (EI): m/z calcd for $C_{38}H_{38}Cl_4Si_2^*$: 690.12607; measured: 690.12641, dev. [ppm]: 0.49, dev. [mmu]: 0.34.

1,3-Bis(1,8-dichloroanthracen-10-yl)-1,1,3,3-tetramethyldisiloxane (8)

Synthesised according to the general procedure using 10-bromo-1,8-dichloroanthracene (**1**; 425 mg, 1.30 mmol), *n*-BuLi solution (0.80 mL, 1.3 mmol) and 1,3-dichlorotetramethyldisiloxane (0.13 mL, 0.67 mmol). Washing the crude product with *n*-pentane (3×3 mL) afforded **10** as a yellow solid; yield: 118 mg (29%).

¹H NMR (500 MHz, CDCl₃): δ = 9.41 (s, 2 H, H9), 8.34 (d, ³*J*_{H,H} = 9.0 Hz, 4 H, H4/H5), 7.49 (d, ³*J*_{H,H} = 7.2 Hz, 4 H, H2/H7), 7.05 (dd, ³*J*_{H,H} = 9.0, 7.2 Hz, 4 H, H3/H6), 0.69 (s, 12 H, 4 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 137.6, 136.5 (C10), 133.2, 129.1, 127.7 (C4/C5), 125.4 (C2/C7), 125.0 (C3/C6), 124.4 (C9), 6.2 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 0.2.

MS (EI, 70 eV): *m*/*z* = 622.2 [M]⁺.

HRMS (EI): *m/z* calcd for C₃₂H₂₆Cl₄OSi₂⁺: 622.02708; measured: 622.02710; dev. [ppm]: 0.03, dev. [mmu]: 0.02.

1,8-Dichloro-10-(dimethylvinylsilyl)anthracene (9)

Synthesised according to the general procedure using 10-bromo-1,8dichloroanthracene (**1**; 408 mg, 1.25 mmol), *n*-BuLi solution (0.85 mL, 1.4 mmol) and dimethylvinylchlorosilane (0.25 mL, 1.8 mmol). Washing the crude product with *n*-pentane (5 mL) afforded **8** as a bright yellow solid; yield: 390 mg (94%).

¹H NMR (500 MHz, CDCl₃): δ = 9.47 (s, 1 H, H9), 8.42 (d, ³*J*_{H,H} = 9.0 Hz, 2 H, H4/H5), 7.61 (d, ³*J*_{H,H} = 7.2 Hz, 2 H, H2/H7), 7.38 (dd, ³*J*_{H,H} = 9.0, 7.2 Hz, 2 H, H3/H6), 6.62 (dd, ³*J*_{H,H} = 20.3, 14.5 Hz, 1 H, SiCH=CH₂), 6.10 (dd, ³*J*_{H,H} = 14.5 Hz, ²*J*_{H,H} = 3.2 Hz, 1 H, SiCH=CH_{cis}H), 5.86 (dd, ³*J*_{H,H} = 20.3, ²*J*_{H,H} = 3.2 Hz, 1 H, SiCH=CH₂), 0.74 (s, 6 H, 2 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 141.1 (SiCH=CH₂), 138.3, 136.2 (C10), 133.3, 131.7 (SiCH=CH₂), 129.3, 128.3 (C4/C5), 125.5 (C2/C7), 125.0 (C3/C6), 124.4 (C9), 2.8 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -11.6.

MS (EI, 70 eV): $m/z = 330.0 \,[M]^+$, 315.0 $[M - CH_3]^+$, 295.0 $[M - Cl]^+$.

HRMS (EI): *m*/*z* calcd for C₁₈H₁₆Cl₂Si⁺: 330.03928; measured: 330.03863; dev. [ppm]: 1.98, dev. [mmu]: 0.65.

10-(Allyldimethylsilyl)-1,8-dichloroanthracene (10)

Synthesised according to the general procedure using 10-bromo-1,8-dichloroanthracene (**1**; 420 mg, 1.29 mmol), *n*-BuLi solution (0.85 mL, 1.4 mmol) and allyldimethylchlorosilane (0.30 mL, 2.0 mmol). Removing traces of 1,8-dichloroanthracene by sublimation (75 °C/0.001 mbar) afforded **9** as a bright yellow solid; yield 276 mg (62%).

¹H NMR (500 MHz, CDCl₃): δ = 9.46 (s, 1 H, H9), 8.33 (d, ³J_{H,H} = 9.0 Hz, 2 H, H4/H5), 7.62 (d, ³J_{H,H} = 7.2 Hz, 2 H, H2/H7), 7.41 (dd, ³J_{H,H} = 9.0, 7.2 Hz, 2 H, H3/H6), 5.79 (ddt, ³J_{H,H} = 16.9, 10.1, 8.1 Hz, 1 H, SiCH₂CH=CH₂), 4.92 (dd, ³J_{H,H} = 16.9 Hz, ²J_{H,H} = 1.9 Hz, 1 H, SiCH₂CH=CHH_{trans}), 4.85 (dd, ³J_{H,H} = 10.1 Hz, ²J_{H,H} = 1.9 Hz, 1 H, SiCH₂CH=CH_{cis}H), 2.17 (d, ³J_{H,H} = 8.1 Hz, 2 H, SiCH₂CH=CH₂), 0.70 (s, 6 H, 2 × CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 138.3, 136.9, 134.4 (CH₂CH=CH₂), 133.4, 129.3, 128.0 (C4/C5), 125.5 (C2/C7), 125.1 (C3/C6), 124.4 (C9), 114.5 (CH₂CH=CH₂), 26.8 (CH₂CH=CH₂), 3.2 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = -4.6.

MS (EI, 70 eV): $m/z = 344.1 \text{ [M]}^+$, 303.1 [M – C₃H₅]⁺, 268.1 [M – C₃H₅ – Cl]⁺.

HRMS (EI): *m*/*z* calcd for C₁₉H₁₈Cl₂Si⁺: 344.05493; measured: 344.05600; dev. [ppm]: 3.10, dev. [mmu]: 1.07.

Photochemical Reactions; General Procedure

In an NMR tube, small amounts (3–5 mg) of the bisanthracenes **2–7** were dissolved or suspended in CDCl₃ (0.5 mL). The mixtures were irradiated with UV light (365 nm) until the reactant was quantitatively converted (monitored by ¹H NMR spectroscopy). When the solvent was dried and degassed bisanthracene **2** yielded the corresponding 9,10:3',4'- photocyclomer **12**. Bisanthracenes **3–7** were not converted at all. In the presence of oxygen and moisture, bisanthracenes **3–7** yielded the anthrone **11**.

1,8-Dichloro-9-hydroxyanthracen-10(9H)-one (11)

This compound was formed from bisanthracenes $\mathbf{3-7}$ as described above in the general procedure.

¹H NMR (500 MHz, CDCl₃): δ = 8.21 (dd, ³*J*_{H,H} = 7.9 Hz, ⁴*J*_{H,H} = 1.3 Hz, 2 H, H4/H5), 7.74 (dd, ³*J*_{H,H} = 7.9 Hz, ⁴*J*_{H,H} = 1.3 Hz, 2 H, H2/H7), 7.51 (t, ³*J*_{H,H} = 7.9 Hz, 2 H, H3/H6), 6.41 (d, ³*J*_{H,H} = 5.7 Hz, 1 H, CHOH), 3.15 (d, ³*J*_{H,H} = 5.7 Hz, 1 H, CHOH).

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¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 182.6 (C=O), 138.4, 135.1 (C2/C7), 135.0, 132.9, 130.2, 126.7 (C4/C5), 61.8 (CHOH).

MS (EI, 70 eV): *m*/*z* = 278.1 [M]⁺, 261.1 [M – OH]⁺, 243.1 [M – Cl]⁺.

HRMS (ESI, + ions): m/z calcd for C₁₄H₈O₂Cl₂Na⁺: 300.97936; measured: 300.9785; dev. [ppm]: 2.86, dev. [mmu]: 0.86.

9,10:3',4' Photocyclomer of Bis(1,8-dichloroanthracen-10-yl)dimethylsilane (12)

This compound was formed from bisanthracene **2** as described above in the general procedure.

¹H NMR (500 MHz, CDCl₃): δ = 8.15 (s, 1 H, H9_a), 7.72 (d, ${}^{3}J_{H,H}$ = 8.2 Hz, 1 H, H5_a), 7.50 (d, ${}^{3}J_{H,H}$ = 7.4 Hz, 1 H, H7_a), 7.40 (t, ${}^{3}J_{H,H}$ = 7.8 Hz, 1 H, H6_a), 7.28 (d, ${}^{3}J_{H,H}$ = 7.1 Hz, 1 H, H4_b), 7.24 (dd, ${}^{3}J_{H,H}$ = 8.1 Hz, ${}^{4}J_{H,H}$ = 1.0 Hz, 1 H, H2_b), 7.13 (dd, ${}^{3}J_{H,H}$ = 7.4, 8.0 Hz, 1 H, H3_b), 6.98 (dd, ${}^{3}J_{H,H}$ = 8.1 Hz, ${}^{4}J_{H,H}$ = 0.8 Hz, 1 H, H7_b), 6.83 (d, ${}^{3}J_{H,H}$ = 7.6 Hz, 1 H, H5_b), 6.67 (t, ${}^{3}J_{H,H}$ = 7.8 Hz, 1 H, H6_b), 6.21 (d, ${}^{3}J_{H,H}$ = 4.0 Hz, 1 H, H2_a), 5.56 (d, ${}^{3}J_{H,H}$ = 2.5 Hz, 1 H, H9_b), 3.95 (d, ${}^{3}J_{H,H}$ = 12.0 Hz, 1 H, H4_a), 3.39 (ddd, ${}^{3}J_{H,H}$ = 12.0, 4.0, 2.5 Hz, 1 H, H3_a), 1.24 (s, 3 H, CH₃), 0.78 (s, 3 H, CH₃).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 146.4, 146.2, 145.9, 142.2, 139.9, 138.0 136.5, 133.7, 131.3, 131.0, 130.7, 130.4, 127.6, 127.3 (C3_b), 127.0 (C2_a), 126.8 (C2_b), 126.8 (C6_a), 126.7 (C6_b), 126.3 (C7_b), 126.2 (C5_a), 126.1 (C7_a), 124.4 (C5_b), 123.2 (C4_b), 121.5 (C9_a), 53.9 (C10_b), 44.8 (C4_a), 43.1 (C9_b), 41.2 (C3_a), 0.2 (CH₃), -2.9 (CH₃).

²⁹Si{¹H} NMR (99 MHz, CDCl₃): δ = 4.9.

MS (MALDI-TOF, + ions, DCTB): $m/z = 548.0 \text{ [M]}^+$, 413.0 [M - Cl]⁺.

HRMS (MALDI-TOF): *m*/*z* calcd for C₂₉H₁₆Cl₄⁺: 548.00829; measured: 548.0074, dev. [ppm]: 1.62, dev. [mmu]: 0.89.

Crystal Structure Determination

Suitable crystals of compounds **2–5** and **7–12** were obtained by slow evaporation of saturated solutions of *n*-pentane (**5**, **9** and **10**), benzene (**3**, **7** and **12**), CH₂Cl₂ (**8**) and CHCl₃ (**2**, **4** and **11**). They were selected, coated with paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a Rigaku SuperNova diffractometer. The structures were refined by fullmatrix least-squares cycles (program SHELXL).¹⁸ Crystal and refinement details, as well as CCDC numbers are provided in Table S2 (SI).¹⁹

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610128.

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